The inherent tensile strength of iron

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ABSTRACT

The cohesive energy of Fe as a function of structure, strain and magnetic state has been computed using the full potential linearized augmented planewave method within the framework of density functional theory and the generalized gradient approximation. Calculations corresponding to uniaxial stress in the <100> direction reveal that the ideal tensile strength of bcc Fe is ~14.2 GPa, and is determined by instability with respect to transformation into an unstable, ferromagnetic fcc. The low-energy fcc phase is a modulated-antiferromagnetic fcc that is connected to bcc via a first-order magnetic transformation, and does not compromise its ideal strength.

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1. INTRODUCTION

The mechanical strength of a crystalline solid is limited by the elastic stability of its crystal lattice (Kelly and Macmillian 1986, Morris and Krenn 2000). The stress that is just sufficient to cause instability forces the crystal to break or deform if it has not already done so, and, therefore, defines the ideal strength. *Ab initio* total energy calculations of the ideal tensile strengths of unconstrained bcc metals show that they are weakest when pulled in a <100> direction (Morris et al. 2000) (unsurprisingly, {100} is the dominant cleavage plane in bcc). There is a simple crystallographic reason for this behavior (figure 1(a)). A relaxed tensile strain along <100> converts the bcc structure into fcc at an engineering strain of about 0.26 (the 'Bain strain'). By symmetry, both structures are unstressed, so the tensile stress must pass through at least one maximum along the transformation path. If we assume a single maximum (the solid line in figure 1(b)) and fit the stress-strain curve with a sinusoid that has the correct modulus at low strain, the ideal tensile strength in <100> is approximately (Morris et al. 2000, Roundy et al. 2001)

$$\sigma_m \sim 0.08E_{100} \qquad (1)$$

in good agreement with *ab initio* calculations (for example, $\sigma_m \sim 30$ GPa for W (Roundy et al. 2001)).

Due to its importance in structural materials, there is an interest in extending this analysis to the case of Fe; however, there is an obvious problem. The above analysis assumes that the fcc phase is unstable with respect to tensile elongation in the <100> direction, whereas the fcc phase in Fe is known to have an energy only slightly above that of bcc, and is at least metastable at low temperature. In fact, the thermomechanical treatments that are used to process structural steel rely on the ease of transforming it from bcc to fcc and back again (Honeycombe and Bhadeshia 1995, Morris et al. 2001a). If we assume a metastable fcc phase connected by a continuous strain-energy curve (the dotted line in figure 1(b)), the tensile instability intrudes at a much smaller strain, and the ideal strength should be only about 6 GPa (versus 12 GPa based on an unstable fcc). This number is too small to be credible. Since tensile stresses that are several times the yield strength are developed ahead of crack tips in elastic-plastic materials (McMeeking and Parks 1979, Morris et al. 2001a), steels with yield strengths much above 1 GPa would necessarily be brittle. In fact, steels with much larger yield strengths have high fracture toughness and considerable ductility (Honeycombe and Bhadeshia 1995).

A possible resolution of this paradox is suggested by the work of Herper et al. (1999). They computed the energies of Fe in various magnetic states and lattice strains. Their calculations suggest that the energy of ferromagnetic Fe increases monotonically if it is distorted toward an unstable, ferromagnetic fcc, which can be stabilized by transforming it into an antiferromagnetic state. We have elaborated on those calculations to clarify their implications for the ideal strength.

2. COMPUTATIONAL METHOD

Specifically, we calculated the ideal strength of Fe within the framework of density functional theory (Hohenberg and Kohn 1964, Kohn and Sham 1965) using WIEN97 (Blaha et al. 1999), a Full Potential Linearized Augmented PlaneWave (FLAPW) code (Singh 1994). We employed the generalized gradient approximation (GGA) (Perdew et al. 1992) for the exchange-correlation energy because it is known to give the correct ferromagnetic bcc groundstate for Fe (Singh et al. 1991). The [Ne]$3s^2$ states were treated as core states using the relativistic Dirac equation, while $3p^6$ $3d^6$ $4s^2$ states were treated as valence states using the scalar-relativistic approximation. We also included 'local orbitals' for the 3d and 3p states to increase the flexibility of the basis set and reduce linearization errors (Singh 1994).

The radius of the 'muffin tin' was 2.0au, with 781 radial mesh points. Our basis set cut-off was at $R_{mt}*K_{max}=10$ and the charge density was expanded up to $G_{max}=14$ $Ry^{1/2}$. The computations were done self-consistently until the energy converged to within 0.01mRy/atom. We used the modified tetrahedron integration method of Blochl et al. (1994) with between 196 and 286 k-points in the irreducible wedge of the Brillouin zone, depending on the particular crystal structure. The total errors, stemming from the choice of basis set, Brillouin zone sampling, and neglect of spin-orbit coupling** are of the order of 0.1mRy/atom.

3. RESULTS

Figure 2 shows the energy and the magnetic moment as functions of volume for the bcc and fcc structures in the non-spin polarized (NM), ferromagnetic (FM) and anti-ferromagnetic (AFM) states. The figure also includes a double period anti-ferromagnetic (DAFM) fcc structure with the spins on (200) planes oriented ↑↑↓↓. This pattern approximates the stable long period spin wave state, as discussed by Herper et al. (1999). The calculations predict the correct ferromagnetic bcc ground state. There is a slight over-binding compared to experiment. The calculated lattice parameter of the bcc phase is 2.827**Å**, approximately 1% smaller than experiment (Acet et al. 1994) while the bulk modulus is 196 GPa, approximately 13% larger than experiment (Rayne and Chandrasekhar 1961). The calculations identify two distinct ferromagnetic fcc phases, one with a small volume and moment and another with larger values of both. The DAFM structure is preferred to either of these, suggesting that the lowest-energy fcc has an intermediate magnetic structure. In fact, small fcc particles of nearly pure Fe can be precipitated from solution in Cu. The fcc crystal has a spiral spin density wave and an energy-volume relation similar to that of the DAFM structure as seen in figure 2 (Tsunoda 1989, Tsunoda et al.1993, Knopfle et al. 2000).

Figure 3(a) shows the lattice energy as a function of engineering strain for a fully relaxed tensile pull in the <100> direction (uniaxial stress), the load configuration that minimizes the ideal tensile strength (Morris et al. 2000, Roundy et al. 2001, Morris et al. 2001b). The figure includes results for the AFM, DAFM, and two FM phases. The results

show that the ferromagnetic bcc phase deforms monotonically toward the high moment fcc FM phase. The strain-energy curve can be fit with a cosine function to within the estimated error of the calculations. The bcc elastic modulus governing a <100> strain ($E_{<100>} = 1/s_{11}$) is given by the second derivative of this curve in the small strain limit, and is 141 GPa, in good agreement with the experimental value of 144 GPa at 4K (Rayne and Chandrasekhar 1961).

The elastic stability of the bcc phase in quasistatic deformation was tested under the thermodynamic criteria derived by Morris and Krenn (2000). Elastic instability occurs at an engineering strain of about 15%, very close to the inflection point on the strain-energy curve. The instability is with respect to deformation in tension, and should, therefore, lead to cleavage fracture. It is associated with the maximum in the Cauchy (true) tensile stress:

$$\sigma = \frac{1}{V}\left\lfloor \frac{dF}{d\varepsilon} \right\rfloor = \frac{1+e}{V}\frac{dF}{de} \qquad (2)$$

where ε (e) is the true (engineering) strain, F is the Helmholtz free energy, and V is the volume (Morris and Krenn 2000). The Cauchy stress is plotted as a function of e in figure 3(b). Its maximum, the ideal tensile strength, is 14.2 GPa, which is reasonably close to the value predicted by equation (1). This is, to our knowledge, the first detailed calculation of the ideal strength of Fe, though other workers have computed the energy for tetragonal structures with various c/a ratios (Herper et al. 2000, Sob et al. 1999), and one of our own co-workers estimated the ideal strength with a modified LDA technique (Roundy and

Cohen 1999). The calculated value is for quasistatic deformation at 0K, and may be decreased by dynamic effects such as soft phonons or spin waves that are not considered here.

The data presented in figure 3(a) show that the three alternate fcc phases considered, the AFM, DAFM and low-spin FM, are related to the equilibrium bcc by first-order phase transformations. Such phases could limit the strength if their energies dropped below that of the parent bcc at small strain, since magnetic transitions might occur and trigger structural instability. However, the AFM, DAFM and low-spin FM states all have energies significantly above that of the high-spin FM state at the point of instability (figure 3(a)). While we have not tested additional complex magnetic structures, the energy of the DAFM structure is only ~1 mRy above that of the non-collinear magnetic ground state of the fcc crystal structure (Herper et al. 1999, Knopfle et al. 2000) while being ~ 6.5 mRy above the high spin FM phase at the point of instability. It is, therefore, likely that Fe remains ferromagnetic to the point of elastic instability.

4. CONCLUSIONS

We conclude that Fe can be strong because its equilibrium bcc phase evolves monotonically toward an unstable ferromagnetic fcc phase when it is strained in the <100> direction, and reaches the limit of stability before the alternate, metastable fcc phases become favored. A delicate balance of crystal and magnetic structure makes it possible for

bcc Fe to have good mechanical strength while simultaneously having the low-energy fcc phase that is so beneficial to its metallurgical processing.

ACKNOWLEDGEMENTS

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division of the U.S. Department of Energy. Computational resources have been provided by the National Energy Research Scientific Computing Center, which is supported by the Office of Energy Research of the U.S. Department of Energy. All Department of Energy support was under Contract No. DE-AC03-76SF00098.

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** While the total energy is lowered by approximately 0.5 mRy/atom when the spin-orbit interaction is included using the second-variational procedure (Singh 1994), the energy difference between the equilibrium bcc phase and the bcc phase at the point of elastic instability is changed by only ~0.12 mRy/atom.

FIGURE CAPTIONS

Figure 1. a) The bcc crystal structure becomes the fcc structure after fully relaxed elongation along the <100> direction. b) The energy as a function of strain has an extremum at the fcc structure which can be a local maximum (solid line) or minimum (dashed line). Assuming sinusoidal form, the inflection point governing the ideal strength falls at a much lower strain in the latter case, and the ideal strength is significantly less.

Figure 2. The energy and magnetic moment per atom as functions of volume for Fe in the bcc (filled symbols) and fcc (open symbols) crystal structures for several magnetic states: non-magnetic (NM) ◆, ferromagnetic (FM) ■, anti-ferromagnetic (AFM) ●, and double period anti-ferromagnetic (DAFM) ▲. The discontinuity in the fcc FM curve separates two distinct phases with different magnetic moments. The energy-volume relation for the ground state spiral spin density wave of fcc Fe (Knopfle et al. 2000) is indicated by the points labeled (+). These are plotted relative to the minimum in the AFM curve to correct for a small, consistent difference in the energies calculated by Knopfle et al. (2000).

Figure 3. a) Energy as a function of fully relaxed engineering strain in the <100> direction for various magnetic phases: high-moment FM ■, low-moment FM ◆, AFM ●, and DAFM ▲. The last data point on the right of each series corresponds to the fcc structure. The different magnetic phases reach the fcc structure at different strains because they have different equilibrium volumes. Some of the energy minima are, in fact, slightly displaced

from fcc because magnetic alignment breaks cubic symmetry (Herper et al. 1999). The bold line fits the high-moment data with the cosine function: 6.0 mRy * [1-cos (π e/.284)]. Elastic instability occurs very close to the inflection point in this curve. b) The Cauchy tensile stress calculated from the cosine fit by equation (2). Its maximum is 14.2 GPa at the tensile instability.